

AD-A127 027

13-DIPOLAR CYCLOADDITION REACTIONS OF LOW VALENT
METAL-CARBONYL COMPLEXES..(U) CALIFORNIA UNIV LOS
ANGELES J A WALKER ET AL. 15 MAR 83 TR-118

1/1

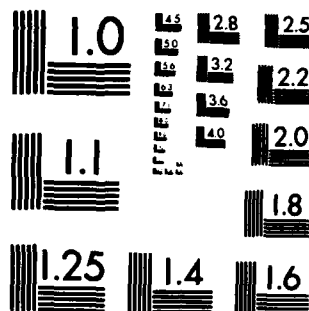
UNCLASSIFIED

N00014-76-C-0390

F/G 7/3

NL

END
DATE
FILMED
5 83
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

12

OFFICE OF NAVAL RESEARCH

Contract No. N00014-76-C-0390

Task No. NR 053-608

TECHNICAL REPORT NO. 118

1,3-DIPOLAR CYCLOADDITION REACTIONS OF LOW VALENT
METAL-CARBONYL COMPLEXES WITH ARYLNITRILE-N-OXIDES

By

John A. Walker, Carolyn B. Knobler and M. Frederick Hawthorne*

Prepared for Publication

in

Journal of the American Chemical Society

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

March 15, 1983

Reproduction in whole or part is permitted
for any purpose of the United States Government

Approved for Public Release; Distribution Unlimited

SELECTED
APR 21 1983
A

AD A127027

DTIC FILE COPY

83 04 20 029

1,3-DIPOLAR CYCLOADDITION REACTIONS OF LOW VALENT
METAL-CARBONYL COMPLEXES WITH ARYLNITRILE-N-OXIDES.

By

John A. Walker, Carolyn B. Knobler and M. Frederick Hawthorne*

Prepared for Publication
in
Journal of the American Chemical Society



Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

A

1,3-DIPOLAR CYCLOADDITION REACTIONS OF LOW VALENT
METAL-CARBONYL COMPLEXES WITH ARYLNITRILE-N-OXIDES.

By

John A. Walker, Carolyn B. Knobler and M. Frederick Hawthorne*

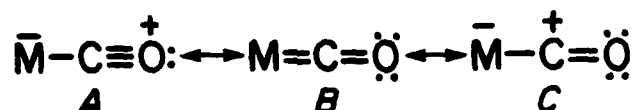
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

ABSTRACT

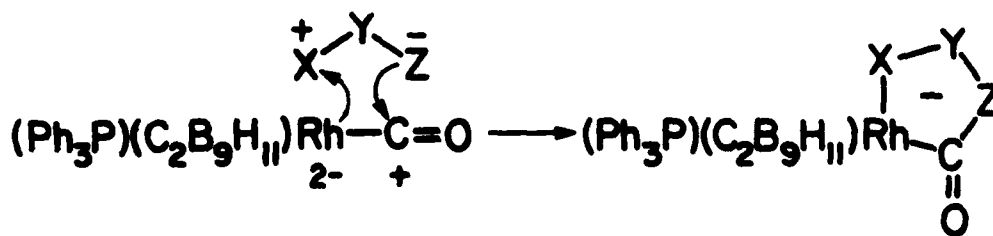
Several low valent metal carbonyl complexes are reported to react with aryl-nitrile-N-oxides to form $(O-N=(Ar)C-M-C(O))$ from a 1,3-dipolar cycloaddition of aryl-nitrile-N-oxide to a $M-C(O)$ bond. Complexes $[Et_4N][(\text{Ph}_3P)(CO)RhC_2B_9H_{11}]$ (1a; 3,1,2 isomer and 1b; 2,1,7 isomer) react with benzonitrile-N-oxide to produce cycloadducts 2a and 2b, respectively. Similarly $K[18\text{-crown-6}]$ 1a and $[Et_4N]$ 1b react with *m*-fluorobenzonitrile-N-oxide to produce 3a and 3b, respectively. Analytical and spectral characterization of the new cycloadducts was supported by the X-ray diffraction study of the $[PPN]^+$ salt of 3b. Reactions of the cycloadducts with CO are described. The complexes $K[18\text{-crown-6}]M(CO)_5$ ($M=Re, Mn$) react with benzonitrile-N-oxide to produce cycloadducts 5a and 5b, respectively. Complex 5a is quite stable, but 5b is exceedingly unstable. $(\eta^5-C_5(CH_3)_5)Rh(CO)_2$ reacts with *p*-chlorobenzonitrile-N-Oxide to produce an intermediate cycloadduct, 8, which can be converted to the known dimeric complex $[(\eta^5-C_5(CH_3)_5)Rh(\mu-CO)]_2$.

Recently chemists have begun to recognize and exploit isolobal^{1a} relationships of C=C and M=C moieties. For example, Stone and coworkers have used this apparent bonding analogy to generate many heteronuclear metal clusters from zero valent platinum reagents or other low valent metal species and Fischer-type carbenes and carbynes.^{1b} While these studies have focused on well defined metal-carbon multiple bonds, another class of metal complexes generally believed to contain metal-carbon multiple bond character², the low valent metal carbonyl complexes, has not received similar attention. We report here a new reaction involving this incipient M=C bond.

Bonding in metal carbonyl complexes can be qualitatively described by A, B and C.



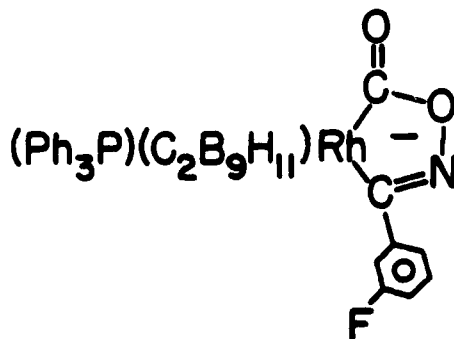
Structures A and C, which do not involve back-bonding, suggest the presence of a nucleophilic metal atom and an electrophilic carbon atom which, when employed together, might lead to reactions of certain metal carbonyl complexes with 1,3-dipolar molecules. Optimally, an electron rich metal carbonyl complex capable of increasing its coordination number from five to six would be expected to be particularly reactive. The two isomeric rhodacarborane anions $[(Ph_3P)(CO)RhC_2B_9H_{11}]^-$ (1a; 3,1,2-isomer and 1b; 2,1,7-isomer), reported in the preceding communication³, possess the key electronic and structural features necessary for such a [3 + 2] cycloaddition reaction. viz:



Indeed the classical 1,3-dipolar molecule, benzonitrile-N-oxide⁴, is reactive towards 1a and 1b; we report the complete characterization of the resultant cycloadducts and the reactivity of several other low valent metal carbonyl complexes towards aryl nitrile-N-oxides.

Dichloromethane solutions of tetraethylammonium salts of 1a and 1b smoothly reacted with 1.3 molar equivalents of benzhydroxamic acid chloride (m.p. 45-48°; caution: skin irritant)⁵ upon warming from -78° to 0°C in the presence of anhydrous K₂CO₃ to produce cycloadducts 2a and 2b, respectively. Complex 2b was isolated as a tetraethylammonium salt (75% yield) by filtration and addition of excess diethylether at 0°. An analytical sample was obtained by recrystallization from CH₃CN/(C₂H₅)₂O at -20° C. Pure NEt₄⁺ salt of complex 2a could not be isolated due to product decomposition. Similarly K[18-crown-6] 1a and NEt₄⁺ 1b react with m-fluorobenzhydroxamic acid chloride to generate analytically pure cycloadducts K[18-crown-6] 3a and NEt₄⁺ 3b. Cycloadducts 2a, 2b, 3a and 3b all display strong absorptions⁶ in the region of 1670-1640 cm⁻¹ (exocyclic C=O) and medium to weak bands in the 1540-1520 cm⁻¹ region (C=N).

An X-ray diffraction study was carried out on the [PPN]⁺ salt of 3b⁷; a projection of the anion is shown in Figure 1. Bond lengths within the metallacycle are not unusual for the valence bond representation shown below which can be described as a 4-rhodaisoxazolin-5-one.



The cycloadducts release carbon dioxide and benzonitrile or *m*-fluorobenzonitrile upon warming. When acetone solutions of the cycloadducts are maintained at 40° C, the pale-yellow color of the metallacycle is replaced by a deep red. The 81.02 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the red solution generated from 3a showed $\text{K}[18\text{-crown-6}][3,3\text{-(Ph}_3\text{P)}_2\text{-3,1,2-RhC}_2\text{B}_9\text{H}_{11}]$ to be the only phosphorus containing species present. The nature of the additional products has not been determined. Complexes 2b and 3b undergo similar thermal decomposition generating $[(\text{C}_2\text{H}_5)_4\text{N}][2,2\text{-(Ph}_3\text{P)}_2\text{-2,1,7-RhC}_2\text{B}_9\text{H}_{11}]$. When the decomposition reaction was performed at 40° C under an atmosphere of CO, both 3a and 3b quantitatively regenerated 1a and 1b, respectively.

The 1,3-dipolar cycloaddition reaction of aryl nitrile-N-oxides could be extended to other low valent metal carbonyl complexes. Slow addition of an ether solution of benzonitrile-N-oxide to a THF solution of $\text{K}[18\text{-crown-6}][\text{Re}(\text{CO})_5]^6$ at -50° C generates a white cycloadduct, 5a,⁶ analogous to 2a. Complex 5a is isolable (60-65%) as a remarkably stable salt, m.p. 155° C (dec). The IR spectrum of 5a indicates that it has the expected metallacyclic structure analogous to 2a or 2b. The reaction of benzhydroxamic acid chloride with $\text{K}[18\text{-crown-6}][\text{Mn}(\text{CO})_5]^6$ in the presence of anhydrous potassium carbonate at -20° C produces the white cycloadduct, 5b.⁶ IR and ^1H NMR spectroscopy indicate that 5b is exactly analogous to 5a; however, due to the low thermal stability of 5b, satisfactory analytical data were not obtained.

Trimethylamine-N-oxide has been commonly used to remove terminal carbonyl ligands (as CO_2), producing unsaturated and reactive metal centers.⁸ For example, the complex $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{CO})_2$ 6, has been converted to the dimeric complex $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\mu\text{-CO})]_2$, 7, by $(\text{CH}_3)_3\text{NO}$ in high yield.⁹ Complex 6 reacts with *p*-chlorobenzonitrile-N-oxide at -40° C to produce yellow-white cycloadduct, 8. Infrared and ^1H NMR spectra indicate that 8 has the anticipated metallacycle structure. Complex 8, thermally unstable (dec. 55° C), slowly produces dimeric complex 7 in solution at 25° C, a transformation which underscores the potential of this methodology for removing coordinated carbon monoxide ligands under exceedingly mild conditions.

Although this report apparently marks the first occasion that a nitrile oxide has been incorporated into a transition metal complex, another class of 1,3-dipolar molecules, aryl and aroyl azides, were long ago reacted with Vaska's complex, trans-(Ph₃P)₂(CO)IrCl, to produce one of the first dinitrogen complexes, trans-(Ph₃P)₂(N₂)IrCl.¹⁰ In light of our current findings, the mode of formation of this iridium-dinitrogen complex may involve 1,3-dipolar addition of the organic azide to the Ir-C(O) dipole in trans-(Ph₃P)₂(CO)IrCl to form a five-coordinate metallacycle (Ph₃P)₂(Cl)ArC(O)N=N=N-Ir-C(O) which subsequently decomposes to the observed products. The formation of the dinitrogen complex, trans-(Ph₃P)₂(N₂)IrCl, was originally proposed¹⁰ to arise from a 1,3-oxidative addition of aroyl azide to the Ir center in trans-(Ph₃P)₂(N₂)IrCl followed by reductive elimination of aroyl isocyanate to generate dinitrogen complex.

The structural characterization of cycloadduct 3b demonstrates the first unequivocal 1,3-dipolar addition to a polarized M=C bond. Decomposition of the cycloadducts described here under mild conditions portends a powerful route to unsaturated, low valent metal complexes and clusters. The utility of this chemistry lies in the exploitation of the unsaturated metal complexes formed by this means and probable application of nitrile oxide reactions to other metal-carbon and metal-metal bonded species. Work in this and related areas continues and will be reported at a later date.

ACKNOWLEDGEMENT:

The authors gratefully acknowledge financial support provided by the Office of Naval Research, (contract #N00014-76-C-0390). We also wish to thank the National Science Foundation for the purchase of the Syntex P1 diffractometer and the Bruker WP-200 NMR spectrometer.

REFERENCES

- 1a. Hoffman, R. Angew. Chem. 1982, 94, 725; see also Nobel Lecture, 1981.
- 1b. Stone, F.G.A.; Accts. Chem. Res. 1981, 14, 318 and references therein.
2. Cotton; Wilkinson; Advanced Inorganic Chemistry, Third Edition, Wiley-Interscience, New York. 1972, p. 684.
3. Walker, J.A.; Knobler, C.B.; Hawthorne, M.F. J. Am. Chem. Soc., 1983, 104, 0000 preceding communication.
4. Huisgen, R.; Angew. Chem. Internat. Ed. 1963, 2, 565 and references therein.
5. Werner, A.; Buss, H. Ber. 1894, 2193.
6. Supplementary Material.
7. Details will accompany the full report.
8. Blumer, D.J.; Barnett, K.W.; Brown, T.L. J. Organomet. Chem., 1979, 173, 71-76, and references therein.
9. Herrmann, W.A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M.L. Angew. Chem. Int. Ed Engl, 1981, 20, 193.
10. Collman, J.P.; Kubota, M.; Vastine, F.D.; Sun, J.Y.; Kang, W. J. Am. Chem. Soc., 1968, 90, 5430, and references therein.

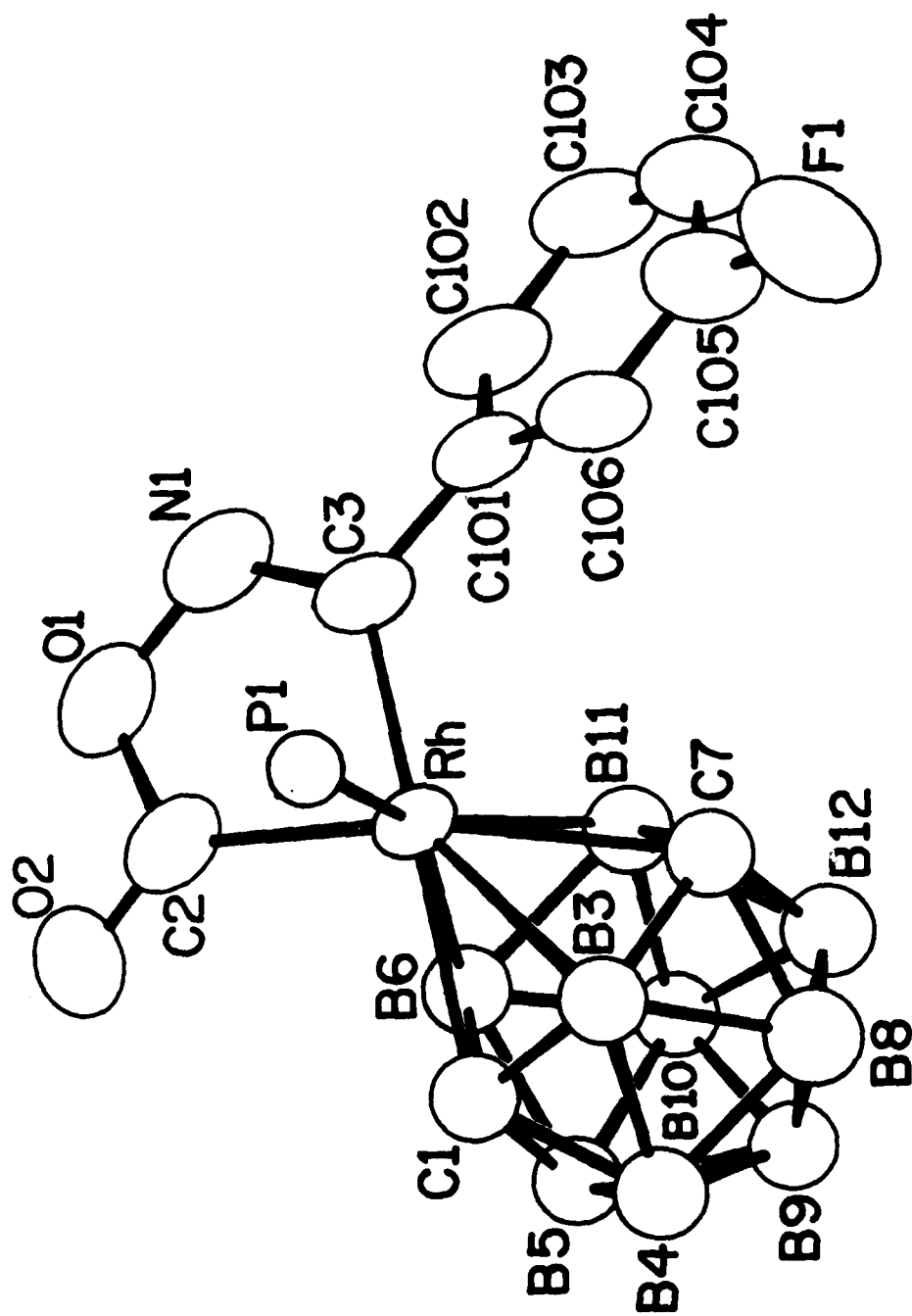


Figure 1.

SUPPLEMENTARY MATERIAL

2a IR (nujol) 1650(s, $\nu_{C=O}$), 1520(m, $\nu_{C=N}$) $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 200K)

26.8 ppm (d, $J_{\text{Rh-P}} = 122$ Hz). (Referenced to external 85% D_3PO_4)

2b Anal. ($\text{C}_{36}\text{H}_{51}\text{N}_2\text{P}_1\text{RhB}_9\text{O}_2$) C, H, P, N, Rh, B. IR (nujol) 1680 (s, $\nu_{C=O}$),

(m, $\nu_{C=N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 200K) 26.5 ppm (d, $J_{\text{Rh-P}} = 120$ Hz).

3a Anal. ($\text{C}_{40}\text{H}_{54}\text{NPRhB}_9\text{FKO}_8$) C, H, N, P, Rh, B, F, K. IR (nujol) 1650

(s, $\nu_{C=O}$), 1520 (m, $\nu_{C=N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 200K) 25.8 ppm

(d, $J_{\text{Rh-P}} = 118$ Hz).

3b Anal. ($\text{C}_{36}\text{H}_{50}\text{N}_2\text{P}_1\text{Rh}_1\text{B}_9\text{F}_1\text{O}_2$) C, H, N, P, Rh, B, F. IR (nujol) 1650 (s, $\nu_{C=O}$),

1520 (w, $\nu_{C=N}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 200K) 24.5 ppm (d, $J_{\text{Rh-P}} = 120$ Hz).

$\text{K}[18\text{-crown-6}][\text{M}(\text{CO})_5]$ (M = Mn, Re) were produced by reduction of the corresponding

$\text{M}_2(\text{CO})_{10}$ complexes in the THF with K(Hg) in the presence of 18-crown-6.

5a Anal. (calcd for $\text{C}_{24}\text{H}_{29}\text{N Re MO}_{12}$) C, H, K, K; Re calcd, 24.87; found 24.39;

Ir(nujol) 1640 cm^{-1} ($\nu_{C=O}$) 1475 cm^{-1} ($\nu_{C=N}$)

5b IR(nujol) 1640 cm^{-1} ($\nu_{C=O}$), 1495 cm^{-1} ($\nu_{C=N}$)

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|-------------------------------------|--|
| 1. REPORT NUMBER 118 | 2. GOVT ACCESSION NO. AD-A127027 | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) "1,3-Dipolar Cycloaddition Reactions of Low Valent Metal-Carbonyl Complexes with Arylnitrile-N-Oxides." | | 5. TYPE OF REPORT & PERIOD COVERED Interim |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s) John A. Walker, Carolyn B. Knobler and M. Frederick Hawthorne* | | 8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0390 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS The University of California Department of Chemistry and Biochemistry Los Angeles, California 90024 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-608 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Branch Office of Naval Research Washington, D.C. 20360 | | 12. REPORT DATE March 15, 1983 |
| | | 13. NUMBER OF PAGES |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | | 15. SECURITY CLASS. (of this report) UNCLASSIFIED |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |
| 16. DISTRIBUTION STATEMENT (of this Report) | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) 1,3 Dipolar Cycloaddition arylnitrile-N-oxides metal carbonyl | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) | | |

DD FORM 1473
1 JAN 73EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102 LF 034 6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

1,3-DIPOLAR CYCLOADDITION REACTIONS OF LOW VALENT
METAL-CARBONYL COMPLEXES WITH ARYLNITRILE-N-OXIDES.

By

John A. Walker, Carolyn B. Knobler and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

ABSTRACT

Several low valent metal carbonyl complexes are reported to react with aryl-nitrile-N-oxides to form $(\text{O}=\text{N}=\text{Ar})\text{C}-\text{M}-\text{C}(\text{O})$ from a 1,3-dipolar cycloaddition of aryl-nitrile-N-oxide to a $\text{M}-\text{C}(\text{O})$ bond. Complexes $[\text{Et}_4\text{N}][(\text{Ph}_3\text{P})(\text{CO})\text{RhC}_2\text{B}_9\text{H}_{11}](\underline{1a}; 3,1,2 \text{ isomer and } \underline{1b}; 2,1,7 \text{ isomer})$ react with benzonitrile-N-oxide to produce cycloadducts 2a and 2b, respectively. Similarly $\text{K}[18\text{-crown-6}] \underline{1a}$ and $[\text{Et}_4\text{N}] \underline{1b}$ react with *m*-fluorobenzonitrile-N-oxide to produce 3a and 3b, respectively. Analytical and spectral characterization of the new cycloadducts was supported by the X-ray diffraction study of the $[\text{PPN}]^+$ salt of 3b. Reactions of the cycloadducts with CO are described. The complexes $\text{K}[18\text{-crown-6}]\text{M}(\text{CO})_5 (\text{M}=\text{Re}, \text{Mn})$ react with benzonitrile-N-oxide to produce cycloadducts 5a and 5b, respectively. Complex 5a is quite stable, but 5b is exceedingly unstable. $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{CO})_2$ reacts with *p*-chlorobenzonitrile-N-Oxide to produce an intermediate cycloadduct, 8, which can be converted to the known dimeric complex $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\mu\text{-CO})]_2$.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|--|-----------------------|---|-----------------------|
| Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217 | 2 | U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709 | 1 |
| ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605 | 1 | Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152 | 1 |
| | 1 | Naval Weapons Center Attn: Dr. A.B. Amster, Chemistry Division China Lake, California 93555 | 1 |
| ONR Branch Office 1030 East Green Street Pasadena, California 91106 | 1 | Naval Civil Engineering Laboratory Attn: Dr. R.W. Drisko Port Hueneme, California 93401 | 1 |
| ONR Branch Office Attn: Dr. L.H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 | 1 | Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940 | 1 |
| Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390 | 1 | Dr. A.L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380 | 1 |
| The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350 | 1 | Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217 | 1 |
| Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360 | 1 | Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401 | 1 |
| Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314 | 12 | Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232 | 1 |
| Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375 | 1 | Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112 | 1 |

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 053

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|--|-----------------------|---|-----------------------|
| Dr. R.N. Grimes Department of Chemistry University of Virginia Charlottesville, Virginia 22901 | 1 | Dr. M.H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401 | 1 |
| Dr. D.B. Brown Department of Chemistry University of Vermont Burlington, Vermont 05401 | 1 | Dr. B. Foxman Department of Chemistry Brandeis University Waltham, Massachusetts 02154 | 1 |
| Dr. W.B. Fox Chemistry Division Naval Research Laboratory Code 6130 Washington, D.C. 20375 | 1 | Dr. T. Marks Department of Chemistry Northwestern University Evanston, Illinois 60201 | 1 |
| Dr. J. Adcock Department of Chemistry University of Tennessee Knoxville, Tennessee 37916 | 1 | Dr. G. Geoffrey Department of Chemistry Pennsylvania State University University Park, Pennsylvania 16802 | 1 |
| Dr. A. Cowley Department of Chemistry University of Texas Austin, Texas 78712 | 1 | Dr. J. Zuckerman Department of Chemistry University of Oklahoma Norman, Oklahoma 73019 | 1 |
| Dr. W. Hatfield Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514 | 1 | Professor O.T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214 | 1 |
| Dr. D. Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139 | 1 | Professor P.S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802 | 1 |
| | | Professor K.M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167 | 1 |
| Professor H. Abrahamson Department of Chemistry University of Oklahoma Norman, Oklahoma 73019 | 1 | Professor R. Neilson Department of Chemistry Texas Christian University Fort Worth, Texas 76129 | 1 |
| Professor M. Newcomb Texas A&M University Department of Chemistry College Station, Texas 77843 | 1 | Professor Richard Eisenberg Department of Chemistry University of Rochester Rochester, New York 14627 | 1 |

FILMED

5-8